

Norbonyl Cations of Group 14 Elements

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Abstract: Norbonyl cations of the group 14 elements Si → Pb have been synthesized from substituted 3-cyclopentenemethyl precursors by intramolecular addition of transient cations to the C=C double bond of the 3-cyclopentenemethyl substituent (π -route to norbonyl cations). The norbonyl cations **4a** (E = Si, R = Me), **4e** (E = Si, R = Et), **4f** (E = Si, R = Bu), **4g** (E = Ge, R = Bu), **4h** (E = Sn, R = Bu), and **4i** (E = Pb, R = Et) have been identified by their characteristic NMR chemical shifts (**4a,e,f**, $\delta(^{29}\text{Si}) = 80\text{--}87$, $\delta(^{13}\text{C})(\text{CH}=\text{C}) = 149.6\text{--}150.6$; **4g**, $\delta(^{13}\text{C})(\text{CH}=\text{C}) = 144.8$; **4h**, $\delta(^{119}\text{Sn}) = 334$, $\delta(^{13}\text{C})(\text{CH}=\text{C}) = 141.5$; **4i**, $\delta(^{207}\text{Pb}) = 1049$, $\delta(^{13}\text{C})(\text{CH}=\text{C}) = 138$). The significant deshielding of the vinylic carbon atoms ($\Delta\delta(^{13}\text{C})$) relative to those of the precursor ($\Delta\delta(^{13}\text{C}) = 19.3\text{--}20.3$ (**4a,e,f**), $\Delta\delta(^{13}\text{C}) = 14.6$ (**4g**), $\Delta\delta(^{13}\text{C}) = 11.1$ (**4h**), $\Delta\delta(^{13}\text{C}) \approx 8$ (**4i**)) and the small J coupling constants between the element and the remote vinyl carbons in the case of **4h** and **4i** ($J(\text{CSn}) = 26$ Hz, $J(\text{CPb}) = 16$ Hz) give experimental evidence for the intramolecular interaction and the charge transfer between the positively charged element and the remote C=C double bond. The experimental results are supported by quantum mechanical calculations of structures, energies, and magnetic properties for the norbonyl cations **4a,b** (E = Ge, R = Me), **4c** (E = Sn, R = Me), **4d** (E = Pb, R = Me), and **4e,f** at the GIAO/B3LYP/6-311G(3d,p)//MP2/6-311G(d,p) (Si, Ge, C, H), SDD (Sn, Pb) level of theory. The calculated ^{29}Si NMR chemical shifts for the silanorbonyl cations **4a,e,f** ($\delta(^{29}\text{Si}) = 77\text{--}93$) agree well with experiment, and the calculated structures of the cations **4a–f** reveal their bridged norbonyl cation nature and suggest also for the experimentally observed species **4a,e–i** a formally $3 + 1$ coordination for the element atom with the extra coordination provided by the C=C double bond. This places five carbon atoms in the close vicinity of the positively charged element atom. The group 14 element norbonyl cations **4a,e–i** exhibit only negligible interactions with the aromatic solvent, and they are, depending on the nature of the element group, stable at room temperature in aromatic solvents for periods ranging from a few hours to days. In acetonitrile solution, the intramolecular interaction in the norbonyl cations **4a,e–h** breaks down and nitrilium ions with the element in a tetrahedral environment are formed. In contrast, reaction of acetonitrile with the plumbyl cation **4i** forms an acetonitrile complex, **10i**, in which the norbonyl cation structure is preserved. The X-ray structure of **10i** reveals a trigonal bipyramidal environment for the lead atom with the C=C double bond of the cyclopentenemethyl ligand and the nitrogen atom of the acetonitrile molecule in apical positions. Density functional calculations at the B3LYP/6-311G(2d,p)//(B3LYP/6-311G(d) (C, H), SDD (Si, Ge, Sn, Pb)) + ΔZPVE level indicate that the thermodynamic stability of the group 14 norbonyl cations increases from Si to Pb. This results in a relative stabilization for the plumbanorbonyl cation **4d** compared to *tert*-butyl cation of 52.7 kcal mol $^{-1}$. In contrast, the intramolecular stabilization energy E_A of the norbonyl cations **4a–d** decreases, suggesting reduced interaction between the C=C double bond and the electron-deficient element center in the plumbacation compared to the silacations. This points to a reduced electrophilicity of the plumbacation compared to its predecessors.

Introduction

Examples of higher homologues of the well-known trivalent carbenium ions, R_3C^+ ,¹ are extremely rare, and only recently some specific examples of silylium, R_3Si^+ ,^{2–5} and germylium, R_3Ge^+ ,^{3c,6} ions in the condensed phase have been synthesized, isolated, and structurally characterized, either by X-ray structure analysis^{3e,5,6} or by NMR methods supported by quantum

mechanical calculations.^{3a–d,4} The evidence for stannylum, R_3Sn^+ , and plumbylum, R_3Pb^+ ,^{7,8} ions with no coordination to counteranions or solvent molecules is rather scarce. The closest approaches to “free” stannylum ions are most probably Lambert’s trimesitylstannylum in benzene using the tetra-

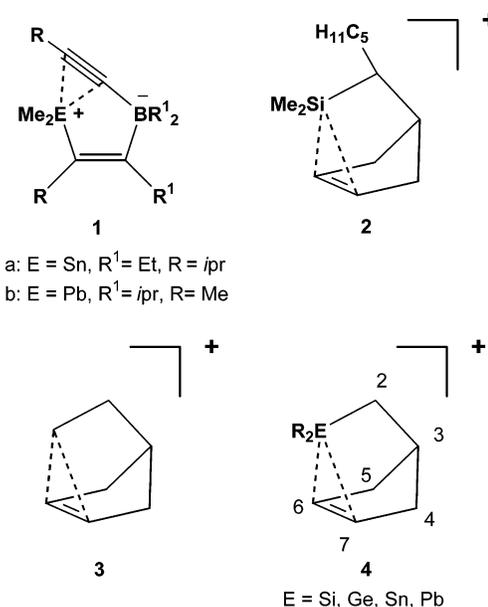
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(2) Reviews: (a) Maerker, C.; Schleyer, P. v. R. In *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 513. (b) Lickiss, P. D. In *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, p 557. (c) Lambert, J. B.; Kania, L.; Zhang, S. *Chem. Rev.* **1995**, *95*, 1. (d) Reed, C. A. *Acc. Chem. Res.* **1998**, *31*, 325. (e) Fornarini, S. In *The chemistry of organic silicon compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 2001; Vol. 3, p 1027.

kispentafluorophenylborate anion^{3b} and Michl's tributylstann-ylidium carboranate.⁹ It is widely accepted that the problems associated with the synthesis of trivalent cations of the elements Si → Pb, R₃E⁺, are due to the high reactivity of these species.² Although thermodynamically more stable than equally substituted carbenium ions, the lower electronegativity of the element compared to carbon results in a high accumulation of positive charge and therefore in an enormous electrophilicity of the R₃E⁺ cations. In addition, the group 14 elements Si → Pb are significantly larger in size. The longer bonds to substituents facilitate access by nucleophiles, and thus higher coordination numbers prevail in the chemistry of silicon and the remainder of the group 14 elements. For example, transient silylium ions, which have been generated by hydride-transfer reactions,¹⁰ readily react with solvents commonly used for ionic compounds such as amines, nitriles, ethers, and aromatic hydrocarbons to form silylated ammonium,¹¹ nitrilium,¹² oxonium,¹³ and arenium¹⁴ ions, respectively. Therefore, the success of the synthesis of these cations requires (i) steric protection of the highly reactive, positively charged silicon³ and/or (ii) an efficient lowering of the electron deficiency of the silicon by either resonance effects or integration of the silicon in aromatic or homoaromatic systems.^{4,5} Alternatively, the high electrophilicity of the positively charged element can be modified by intramo-

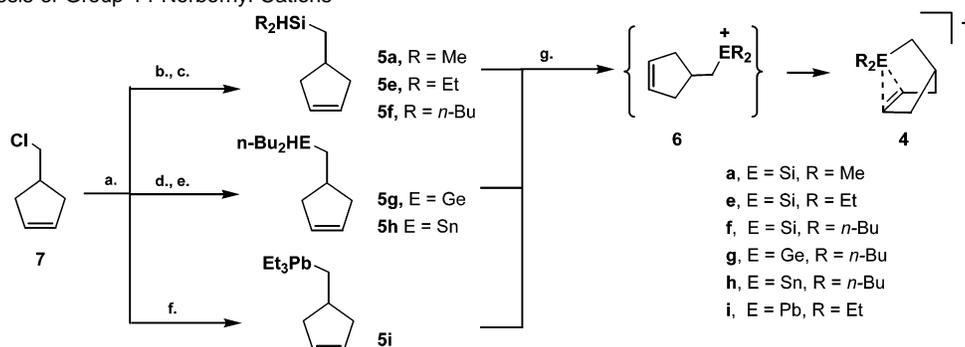
lecular donation from remote donor substituents. This interaction leads to solvent-free cations with coordination numbers for the positively charged element >3 and to a considerable electron transfer from the donor group to the element. Frequently used donor substituents utilize heteroatoms with lone pairs (e.g., amino, hydrazino, methoxy, carboxy, phosphino, etc.)¹⁵ for the stabilization of the cationic center. We have previously shown that the intramolecular reaction between transient silylium ions and C≡C triple bonds or aryl groups leads to the clean formation of silyl-substituted vinyl cations¹⁶ or silylated arenium ions.¹⁷ Wrackmeyer and co-workers synthesized and characterized the intriguing zwitterions **1** by X-ray analysis, in which trivalent stannylum and plumbylum ions are stabilized by intramolecular side-on coordination to C≡C triple bonds. Alternatively, these ions can be regarded as stannyl- or plumbyl-substituted vinyl cations. The usability of C=C double bonds for the intramolecular stabilization of a transient silyl cation was demonstrated using a cyclopentenemethyl-substituted precursor, yielding silanorbonyl cation **2**¹⁹ along the so-called π-route to norbornyl cations.²⁰ According to quantum mechanical calculations,^{2a,19} silanorbonyl cation **2** adopts a symmetrically bridged structure, with the silicon atom in a pentacoordinate bonding situation, similar to that of the parent norbornyl cation **3**.^{1b,c,21}

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The success of this previous work¹⁹ prompted us to use the 3-cyclopentenemethyl substituent also for the synthesis of intramolecularly stabilized cations of the heavier group 14 elements, **4**. This series of group 14 element norbornyl cations provides a unique opportunity to gauge the different electrophilicities of the positively charged group 14 centers in a similar

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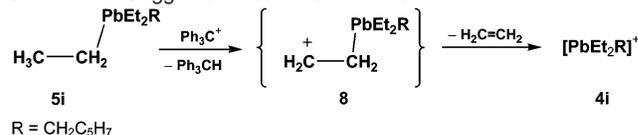
Scheme 1. Synthesis of Group 14 Norbornyl Cations^a

^a Reagents and conditions: (a) Mg, THF; (b) HSiCl₃, THF, -15 °C to room temperature; (c) RMgCl, THF; 0 °C to room temperature; (d) *n*-Bu₂EtCl₂, THF, 0 °C to room temperature; (e) (E = Ge) LiAlH₄, Et₂O, room temperature; (E = Sn) LiEt₃BH, Et₂O, room temperature; (f) Et₃PbBr, Et₂O, room temperature; (g) TPFPB, C₆D₆, room temperature.

molecular environment. We describe herein the synthesis of norbornyl cations of the group 14 elements under experimental conditions that allow their NMR characterization in solution at ambient temperature. The results of quantum mechanical investigations on the structures, energies, and magnetic properties are reported; these not only corroborate the experimental findings but also give a detailed description of the bonding and charge distribution in the norbornyl cations.

Results and Discussion

Experiment. The norbornyl cations **4a,e–h** are synthesized by hydride-transfer reactions between trityl cation and the respective element hydrido compounds **5a,e–h**.¹⁰ Due to the instability of lead(IV) hydrido compounds, the plumbyl cation **4i** is prepared by reaction of the triethyl-substituted plumbane **5i** with trityl cation (Scheme 1). The compounds **5a,e–i** are obtained from cyclopentenemethyl chloride, **7**, and the corresponding element halides by the reactions summarized in Scheme 1. The structures of compounds **5a,e–i** are verified by using standard one-dimensional ¹H, ¹³C, ²⁹Si, ¹¹⁹Sn, and ²⁰⁷Pb and two-dimensional ¹H/¹³C and ¹H/¹H NMR techniques. Treatment of **5a,e–i** with 1 equiv of trityltetrakis(pentafluorophenyl)borate (TPFPB) in benzene-*d*₆ or toluene-*d*₈ gives in the first step the triorgano-substituted element cations **6a,e–i**

Scheme 2. Suggested Mechanism for the Formation of **4i**

and the byproduct triphenylmethane; this last compound is unequivocally identified from its ¹H and ¹³C NMR spectra.²² The cations **6a,e–i** are transient species and undergo an intramolecular reaction, yielding the norbornyl cations **4a,e–i** (Scheme 1).

The preparation of the plumbyl cation **4i** is rather unusual,²³ and the reaction is suggested to proceed via β-hydride abstraction from the ethyl ligand of **5i** (Scheme 2). Deplumbylation of the resulting β-plumbyl-substituted carbocation **8** results in the formation of the norbornyl cation **4i** and ethene. The byproducts ethene and triphenylmethane were identified by ¹H and ¹³C NMR spectroscopy.^{22,24} Another byproduct, the arenium ion, [Et₃Pb/C₆D₆]⁺, arises from elimination of ethene from tetraethyllead, Et₄Pb. The latter compound is formed from **5i** by a fast ligand disproportionation reaction.²⁵ In our experience, even freshly distilled samples of **5i** are contaminated by traces of tetraethyllead. Therefore, triethyllead benzenium, [Et₃Pb/C₆D₆]⁺, is an unavoidable byproduct of **4i**. The identity of [Et₃Pb/C₆D₆]⁺ was established by its independent synthesis from tetraethyllead and TPFPB in benzene (see the Experimental Section).

Solutions of norbornyl cations **4a,e–i** in aromatic hydrocarbons are stable at room temperature; however, there is a clear dependence of the stability on the element and on the substituents at the element. The dimethylsilanorbornyl cation **4a** decomposes completely within hours, while the butyl-substituted species **4f** can be handled over the same period of time without observable disintegration. The stannanorbornyl cation **4h** can be shortly heated to 70 °C without noticeable decomposition, and the plumbanorbornyl cation **4i** is at room temperature indefinitely stable in the absence of strong nucleophiles and

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Table 1. NMR Data of Group 14 Element Norbonyl Cations^a

compd	E	R	$\delta(E)$	$\Delta\delta(E)^b$	$\delta(^{13}C)(C6/7)$	$\Delta\delta(^{13}C)(C6/7)^c$	$\delta(^{13}C)(C4/5)$	$\delta(^{13}C)(C3)$	$\delta(^{13}C)(C2)$	$\delta(^{13}C)(R)$
4a	Si	Me	87.2	102.1	150.6	20.3	41.4	37.4	14.5	-2.2
			87.5 ^d		¹ J(CH) = 170.4					
4e	Si	Et	82.7	86.4	149.8	19.5	41.6	36.5	10.4	5.3, 6.1
			83.0 ^d		¹ J(CH) = 173.0					
4f	Si	<i>n</i> -Bu	80.2	89.4	149.6	19.3	41.6	36.6	12.7	13.0, 25.4, 24.9, 12.6
					¹ J(CH) = 174.1					
4g	Ge	<i>n</i> -Bu			144.8	14.6	40.4	36.5	18.2	18.5, 24.8, 25.8, 12.4
					¹ J(CH) = 173.2					
4h	Sn	<i>n</i> -Bu	334.0	343.0	141.5	11.1	40.4	35.3	25.0	19.9, 27.6, 26.2, 12.4
					¹ J(CH) = 170.0					
4i	Pb	Et	329.7 ^d	999.0	138.0	7.8	39.3	36.5	53.4	38.2, 12.0
			1049.0		¹ J(CSn) = 26					
					¹ J(CH) = 170.0					
			1039.0 ^d		¹ J(CPb) = 16					
10a	Si	Me	31.8		130.0	0.0	41.4	32.6	21.8	-2.5
10e	Si	Et	37.5		129.5	-0.6	41.0	32.1	17.8	5.2, 3.7
10f	Si	<i>n</i> -Bu	37.5		130.7	0.4	41.0	32.0	18.7	12.5, 25.4, 23.8, 10.9
10g	Ge	<i>n</i> -Bu			130.6	0.4	40.2	33.2	17.5	12.6, 25.7, 25.1, 24.5
10h	Sn	<i>n</i> -Bu	54.4		130.7	0.3	42.5	35.1	19.5	13.3, 28.3, 26.9, 19.5
10i	Pb	Et	598.0		131.7	1.5	40.9	35.6	49.1	34.3, 12.0

^a In benzene-*d*₆ at room temperature versus TMS, coupling constants *J* in hertz. ^b Chemical shift difference for the element between the cations **4** and their precursors **5**. ^c Chemical shift difference for the vinylic carbon atoms C6/7 in the cations **4** and **10**, respectively, and in the precursors **5**. ^d In toluene-*d*₈.

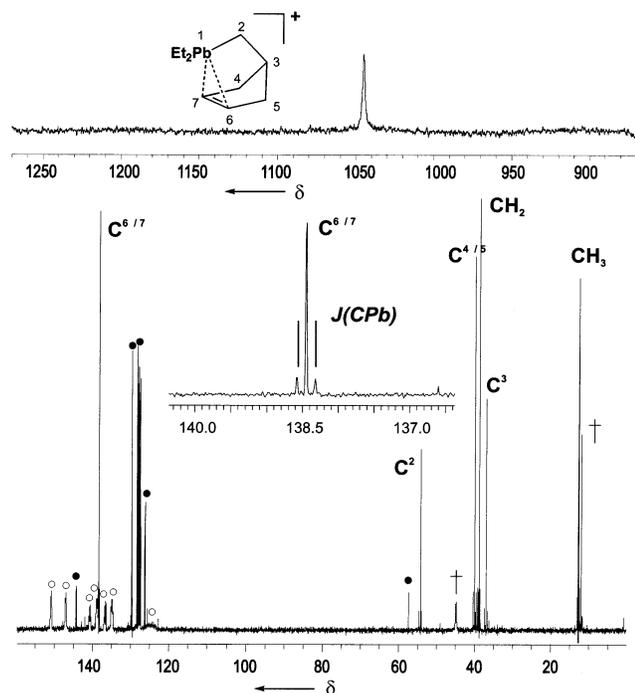


Figure 1. NMR spectra of plumbanorbonyl cation **4i** at 300 K in benzene-*d*₆: (a) 52.3 MHz ²⁰⁷Pb NMR spectrum; (b) 63 MHz ¹³C NMR spectrum (†, [Et₃Pb/C₆D₆]⁺; ○, [B(C₆F₅)₄]⁻; ●, Ph₃CH). Inset: part of the ¹³C DEPT-135 NMR spectrum, showing the resonance of the vinylic carbon atoms.

air. The norbonyl cation salts with [B(C₆F₅)₄]⁻ as counterion have been obtained as brown-red glassy powders after removal of the solvent. Treatment of the residue with pentane yields brown-red (**4a,e–g**) or white microcrystalline (**4h,i**) salts in 60–95% yield.²⁶

The norbonyl cations **4a,e–i** (Table 1) were identified by their characteristic NMR spectra (see Figure 1, for an example). The strong downfield shift of the element NMR signal ($\Delta\delta(E)$)

of all cations **4a,e–i** ($\Delta\delta(^{29}\text{Si}) = 86.4–102.1$, $\Delta\delta(^{119}\text{Sn}) = 343$, $\Delta\delta(^{207}\text{Pb}) = 999$), which occurs upon ionization of the precursors **5a,e–i**, indicates an accumulation of positive charge at the element atom. The observed ²⁹Si NMR chemical shifts for the silyl cations **4a,e,f** ($\delta(^{29}\text{Si}) = 80.2–87.2$), the ¹¹⁹Sn NMR chemical shift for the stannyl cation **4h** ($\delta(^{119}\text{Sn}) = 334$), and the ²⁰⁷Pb NMR chemical shift for the plumbyl cation **4i** ($\delta(^{207}\text{Pb}) = 1049$) are similar to chemical shifts found for metalated benzenium ions ($\delta(^{29}\text{Si}) = 70–100$,^{14b,27} $\delta(^{119}\text{Sn}) = 360$,^{8b} $\delta(^{207}\text{Pb}) = 1432$),²⁸ and they are markedly smaller than the chemical shifts reported for trivalent cations ($\delta(^{29}\text{Si}) = 225$ (Mes₃Si⁺),^{3a,f} $\delta(^{119}\text{Sn}) = 806$ (Mes₃Sn⁺).^{3b}

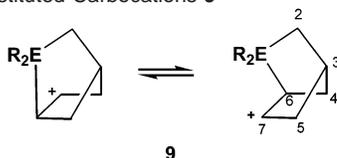
For all norbonyl cations nearly the same NMR chemical shifts are observed in benzene-*d*₆ solution and in toluene-*d*₈, that is, NMR chemical shift changes of less than 1% (see Table 1). For silylated or stannylated arenium ions, chemical shift differences between the benzenium and toluenium species of 10% and more are reported ([Et₃SiC₆D₆]⁺, $\delta = 92.3$; [Et₃SiC₆D₅CD₃]⁺, $\delta = 81.8$;²⁷ [Bu₃SnC₆D₆]⁺, $\delta = 360$;^{8b} [Bu₃SnC₆D₅CD₃]⁺, $\delta = 434$).²⁹ This indicates negligible solvent–cation interactions for the norbonyl cations **4a,e–i** in aromatic solvents. For the cations **4a,e–i** the saturated backbone carbon atoms, C3–C5, show the same ¹³C NMR chemical shift pattern, which is typical for the norbonyl cage. Only the chemical shift of methylene carbon atom C2 is influenced by the element substitution and varies for each cation (see Table 1). The ¹³C NMR chemical shifts for the vinylic carbons C6 and C7 are in the range of 138.0–150.2 and are highly diagnostic of the bridged structure of the ions. The marked downfield shifts of C6/7, $\Delta\delta(^{13}C)(C6/7)$, relative to those of the precursor compounds ($\Delta\delta(^{13}C)(C6/7) = 7.8–20.5$) are consistent with intramolecular coordination of the double bond to the positively charged element and indicate charge transfer from the element

(27) Lambert, J. B.; Zhang, S.; Ciro, S. M. *Organometallics* **1994**, *13*, 2430.

(28) [Et₃Pb/C₆D₆]⁺[B(C₆F₅)₄]⁻ in C₆D₆ at room temperature; see the Experimental Section.

(29) Blackwell, J. M.; Piers, W. E.; McDonald, R. *J. Am. Chem. Soc.* **2002**, *124*, 1296.

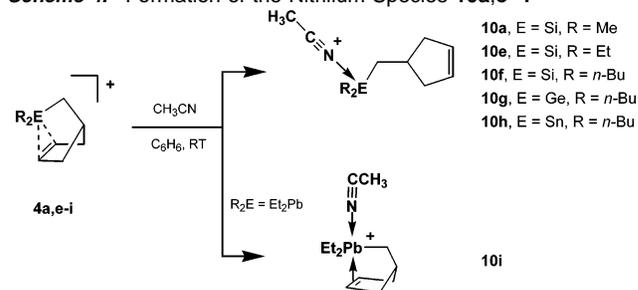
(26) In the case of the norbonyl cation salts **4h**[B(C₆F₅)₄] and **4i**[B(C₆F₅)₄] suitable crystals for X-ray analysis have been obtained; the crystal structure could however not be resolved because of severe disordering of the cations.

Scheme 3. Degenerate Equilibrium between Two β -Element-Substituted Carbocations **9**

to the carbon atoms C6/7.¹⁹ While the downfield shift $\Delta\delta(^{13}\text{C})$ -(C6/7) for the silanorbornyl cations **4a,e,f** is nearly constant, about 20, it decreases for the germanorbornyl (**4g**; $\Delta\delta(^{13}\text{C})$ -(C6/7) = 14.6) and stannanorbornyl (**4h**; $\Delta\delta(^{13}\text{C})$ -(C6/7) = 11.1) cations and reaches for the plumbanorbornyl cation **4i** its minimum value of 7.8. This implies reduced electron transfer from the C=C double bond to the element in the series Si \rightarrow Pb.

The small detected J coupling constants between the element and the vinylic carbon atoms for both the stannyl cation **4h** and the plumbyl cation **4i** ($^1J(\text{SnC}) = 26$ Hz, $^1J(\text{PbC}) = 16$ Hz) demonstrate the direct bonding of the element to the C=C double bond, since the alternative coupling path along four bonds cannot lead to substantial scalar coupling.^{30,31} The observed $^1J(\text{EC})$ values are by magnitudes smaller than regular couplings along a C–E single bond ($^1J(\text{SnC}) = 300\text{--}500$ Hz, $^1J(\text{PbC}) = 200\text{--}300$ Hz),^{30,31} a fact which can be rationalized by the particular bonding situation in these cations. Similar strongly reduced $^1J(\text{SnC})$ and $^1J(\text{PbC})$ constants have been found for zwitterionic compounds of type **1** ($^1J(\text{CPb}) = 11\text{--}30$ Hz,^{18e} $^1J(\text{CSn}) = 40\text{--}74$ Hz)^{18a–d} in which the R_3E^+ (E = Sn, Pb) units are coordinated to a C \equiv C triple bond. Additional independent indication for a 3 + 1 coordination of the tin atom in **4h** is provided by the relatively small $^1J(\text{CSn})$ of 256 Hz for coupling to the methylene groups of the butyl substituents. This coupling constant is clearly reduced compared to that of the tetrahedral coordinated tin center in stannane **5h** ($^1J(\text{SnC}) = 342$ Hz) and to the pentacoordinated tin atom in stannyl cations (i.e., in $\text{Bu}_3\text{Sn}(\text{DMSO})_2$ $^1J(\text{SnC}) \approx 465$ Hz).^{8d,32} However, it is similar to the corresponding coupling constants in the stannylated benzenium ion $[\text{Bu}_3\text{Sn}/\text{C}_6\text{H}_6]^+$ ($^1J(\text{SnC}) = 278$ Hz)^{8d} and in the zwitterionic species **1a** ($^1J(\text{SnC}) = 233\text{--}295$ Hz).^{18a–d} For both types of compounds the 3 + 1 coordination of the tin atom is established.^{8d,18b,c}

The NMR spectra of the cations **4a,e–i** are consistent with a symmetrical norbornyl cation structure, and also low-temperature NMR studies at -40 °C in toluene- d_8 showed no kinetic line broadening of the ^{13}C NMR signals.³³ This indicates the absence of a conceivable degenerate equilibrium between two β -element-substituted carbocations **9** (Scheme 3). An analysis of the NMR data (Table 1) provides further evidence for the static, bridged structure of the norbornyl cations and negates an equilibrating system, **9**: (i) The $^1J(\text{CH})$ coupling constants of the vinylic methine carbons in the norbornyl cations **4** are 170–174 Hz. This is close to the value obtained for the parent norbornyl cation **3** ($^1J(\text{CH}) = 187.7$)^{20b} and decisively larger than the time-averaged coupling constants $J^{\text{av}} \approx 150$ Hz expected for fast equilibrating cations **9**.³⁴ (ii) In contrast, the time-averaged $^1J(\text{EC})$ coupling constants for cations **9h,i** are

Scheme 4. Formation of the Nitrilium Species **10a,e–i**

expected to be larger than 100 Hz (E = Pb) or 150 Hz (E = Sn).³⁶ This is more than a magnitude larger than the detected $^1J(\text{EC})$ coupling constants in **4h** and **4i** (**4h**, $^1J(\text{SnC}) = 26$ Hz; **4i**, $^1J(\text{PbC}) = 16$ Hz).

The addition of solvents that are stronger coordinating agents to positively charged centers than aromatic hydrocarbons leads to the immediate collapse of the intramolecular E/C=C interaction. Thus, the addition of acetonitrile to a solution of the norbornyl cations **4a,e–h** in benzene or toluene instantaneously gives the nitrilium species **10a,e–h**, which are unequivocally identified by their characteristic element and ^{13}C NMR spectra (see Scheme 4 and Table 1).¹² In the nitrilium ions **10a,e–h** no noticeable interaction between the element and the C=C double bond is present; that is, the ^{13}C NMR chemical shifts of the vinylic carbons are nearly identical to those of the precursor silanes **5** ($\Delta\delta(^{13}\text{C}) \approx 0$; see Table 1).

The markedly high field shifted ^{207}Pb NMR resonance for cation **10i** ($\delta(^{207}\text{Pb}) = 598$ relative to $\delta(^{207}\text{Pb}) = 1049$ for **4i**) indicates also for this compound strong coordination of the acetonitrile to the lead atom. The ^{13}C NMR signals of the vinylic carbons for **10i** are however still at higher field than for the starting plumbane **5i** ($\Delta\delta(^{13}\text{C}) = 1.5$; see Table 1). This small but significant effect on $\delta(^{13}\text{C})$ (=CH) suggests a residual interaction between the C=C double bond and the lead atom and therefore pentacoordination of the lead center in **10i** (see Scheme 4). This is supported by the solid-state structure of the salt **10i** $[\text{B}(\text{C}_6\text{F}_5)_4]$.³⁷ The structure of the salt reveals well-separated cations and anions. No fluorine atom of the anion approaches the lead atom at a smaller distance than 380 pm. In agreement with the NMR data, obtained for **10i** in solution, the molecular structure of **10i** reveals a distorted pentagonal bipyramidal environment for the lead center (see Figure 2). The planarity of the trigonal base is indicated by summation of the three C–Pb–C angles (118.0°, 119.9°, and 122.1°) to 360.0°. The coordination sphere of lead is completed by the C=C double bond of the cyclopentenemethyl substituent and one acetonitrile molecule which take up the two apical positions. The steric requirements of the intramolecular interaction between the C=C double bond and the lead atom enforces the deviations from the ideal trigonal bipyramidal coordination. That is, (i)

(34) Calculated from $^1J(\text{C}^+-\text{H}) = 170$ Hz and $^1J(\text{C}^+-\text{H}) = 130$ Hz in secondary carbocations.³⁵

(35) (a) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 5026. (b) Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C NMR Spektroskopie*; Thieme: Stuttgart, Germany, 1984.

(36) Calculated using the coupling data from $n\text{-Bu}_4\text{Sn}$ ($^1J(\text{CSn}) = 314$ Hz, $^2J(\text{CSn}) = 20$ Hz) and $n\text{-Bu}_4\text{Pb}$ ($^1J(\text{CPb}) = 189$ Hz, $^2J(\text{CPb}) = 27$ Hz).

(37) Crystal data for **10i** $[\text{B}(\text{C}_6\text{F}_5)_4]$ at 173 K: empirical formula $\text{C}_{36}\text{H}_{22}\text{BF}_5\text{Pb}$, MW = 1066.55, orthorhombic, space group $Pbca$, $a = 17.1043(5)$ Å, $b = 19.7079(6)$ Å, $c = 22.3659(8)$ Å, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 7539.3(4)$ Å³, $Z = 8$, D_{calc} = 1.879 Mg/m³. The final R factor was 0.0353 with $I_0 > 2\sigma(I_0)$ ($R_w = 0.059$ for all data, 10755 reflections), GOF = 1.021. Cambridge database file CCDC-190293.

(30) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

(31) Wrackmeyer, B.; Horchler, K. *Annu. Rep. NMR Spectrosc.* **1989**, *22*, 249.

(32) Nadvornik, M.; Holecck, J.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* **1984**, *275*, 43.

(33) At lower temperatures even the toluene solution of the salt becomes solid.

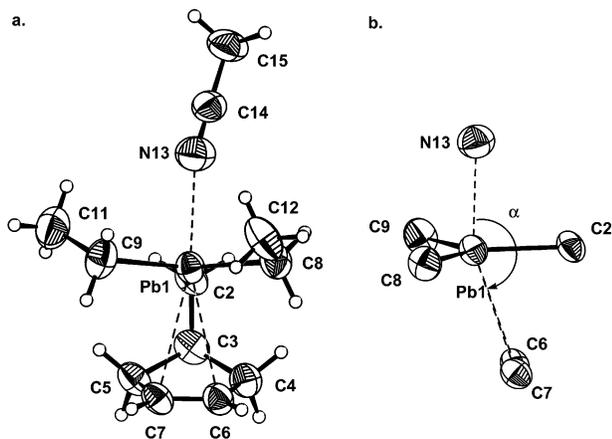


Figure 2. (a) Molecular structure of cation **10i** in the crystal. (b) Coordination sphere of the lead atom in cation **10i**. Selected bond lengths (pm) and bond angles (deg): Pb1–C2 222.3(4); Pb1–C8 221.9(5); Pb1–C9 221.4(4); Pb1–C6 298.9(4); Pb1–C7 296.9(5); Pb–(center C6, C7) 290.4; Pb1–N13 250.6(5); C6–C7 132.7(5); C6–Pb–C7 25.7(9); C2–Pb–C8 119.88(15); C2–Pb–C9 122.10(16); C8–Pb–C9 117.99(16); (center C6,C7)–Pb–N13 159.0; (center C6,C7)–Pb–C2 72.3; N13–Pb–C2 86.80(14).

the axis along the center of the C=C double bond and the lead atom is tilted by 17.7° toward the C2Pb1 axis and (ii) the midpoint of the C=C double bond and the nitrogen atom enclose an angle α with the central lead atom, which differs markedly from 180° ($\alpha = 159.0^\circ$; see Figure 2). This spatial arrangement places six atoms at distances smaller than 300 pm around the positively charged lead atom.

Theory. Calculations³⁸ of the structures and energies of norbornyl cations and related compounds were initially performed using the nonlocal DFT level of theory³⁹ and Becke's three-parameter hybrid functional and the LYP correlation functional (B3LYP),⁴⁰ along with the standard 6-31G(d) for C and H. For the elements Si \rightarrow Pb the Stuttgart–Dresden pseudorelativistic effective core potential (ecp)^{41,42} along with a (31/31/1) valence basis set has been used (B3LYP/6-31G(d) (C, H), SDD (E)). Subsequent frequency calculations at the B3LYP/6-31G(d) (C, H), SDD (E) level were carried out to verify stationary points as minima on the potential energy surface (PES). For the silanorbornyl cation **4a** calculations using the same method, but the all-electron 6-31G(d) basis set also for the element, have been done for comparison. While only minor differences in the relative energies have been found for calculations utilizing the all-electron basis set and the ecp calculations,⁴³ the geometries, in particular the distances between the elements and the C=C double bond, crucially depend on the applied basis set and the method (see Figure 3 for an example). Finally, relative energies were calculated at the

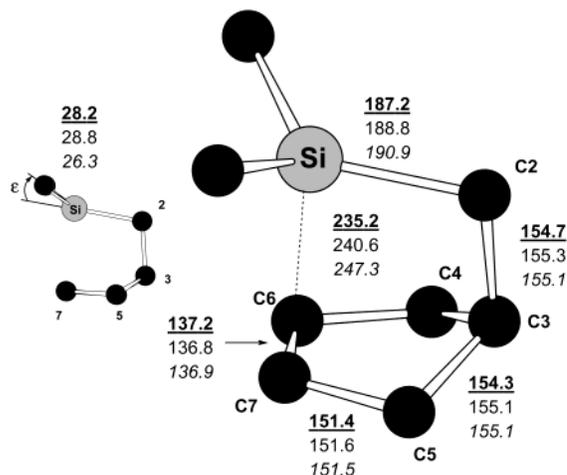


Figure 3. Calculated structure of cation **4a** at several levels of theory (bold, MP2/6-311G(d,p); lightface Roman, B3LYP/6-31G(d); lightface italic, B3LYP/(6-31G(d), (C, H), SDD (Si))). Bond lengths are in picometers. The pyramidalization angle ϵ is in degrees.

Table 2. Calculated Stabilization Energy of Me_3E^+ vs *tert*-Butyl Cation (Eq 1) and of Element Norbornyl Cations **4** vs Me_3E^+ (Eq 2) and the Intramolecular Stabilization Energy E_A (kcal mol⁻¹, at the B3LYP/6-311G(2d,p) (C, H), SDD (E) + ΔZPVE Level)

	Si	Ge	Sn	Pb
eq 1	-12.0	-20.6	-25.6	-35.2
eq 2	-23.8	-21.5	-21.6	-17.5
E_A	-19.5	-17.4	-17.0	-12.5

B3LYP/6-311G(2d,p) level with B3LYP/6-31G(d) geometries, and those energies were further improved by addition of unscaled zero-point vibration energy differences (ΔZPVE) (B3LYP/6-311G(2d,p) (C, H), SDD (E))/B3LYP/6-31G(d) (C, H), SDD (E) + ΔZPVE). Relative energies, reaction energies, and association energies E_A quoted in the text are computed at this level, unless otherwise stated. ¹³C and ²⁹Si NMR chemical shifts have been calculated using the GIAO⁴⁴/B3LYP method, the 6-311G(3d,p) basis set, and geometries optimized at MP2/6-311G(d,p).⁴⁵ The electron distributions in cations **4** were analyzed using NBO theory⁴⁶ and a B3LYP/6-31G(d) density.

Thermodynamic Stabilities of Group 14 Element Cations.

From the decreasing Mulliken electronegativity of the group 14 elements (Si \rightarrow Pb) it is expected that the thermodynamic stability of the trivalent ER_3^+ species advances continuously from silylium to plumbylum ions.^{7a,b} This trend is paralleled by a reduced electrophilicity of the R_3E^+ cations, which is due to the increasing polarizability of the element atoms.^{7a} These qualitative conclusions are supported by the results of density functional calculations (B3LYP/6-311G(2d,p) (C, H), SDD (E))/B3LYP/6-31G(d) (C, H), SDD (E)). According to the isodesmic equation⁴⁷ (eq 1) (see Table 2), the stabilization energy versus *tert*-butyl cation increases significantly in the series $\text{Me}_3\text{Si}^+ \rightarrow \text{Me}_3\text{Pb}^+$.⁴⁸ The results for the isodesmic reaction, which is

(38) All calculations were performed with Gaussian 94, Revisions C2–E2, and Gaussian 98, Revisions A3–A9, Gaussian, Inc., Pittsburgh, PA, 1995 and 1999.

(39) (a) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: Oxford, 1989. (b) Koch, W.; Holthausen, M. C. *A Chemist's Guide to Density Functional Theory*; Wiley-VCH: Weinheim, Germany, 2000.

(40) (a) Becke, A. D. *Phys. Rev.* **1988**, *A 38*, 3098. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (c) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(41) Cundari, T. R.; Benson, M. T.; Lutz, M. L.; Sommerer, S. O. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; VCH: New York, 1996; Vol. 8, p 145.

(42) Quasirelativistic effective core potentials (ECPs): (a) Bergner, A.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1993**, *80*, 1431. (Si, Ge, Sn). (b) Kuechle, W.; Dolg, M.; Stoll, H.; Preuss, H. *Mol. Phys.* **1991**, *74*, 1245. (Pb).

(43) For example, the relative energy of **4a** versus **6a** is 22.7 kcal mol⁻¹ (B3LYP/6-31G(d) (C, H), SDD (Si))/B3LYP/6-31G(d) (C, H), SDD (Si), 23.9 kcal mol⁻¹ (B3LYP/6-31G(d))/B3LYP/6-31G(d), or 28.7 (MP2/6-311G(d,p))/MP2/6-311G(d,p).

(44) (a) Ditchfield R. *Mol. Phys.* **1974**, *27*, 789. (b) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1982**, *104*, 5667. (c) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

(45) (a) Møller C.; Plesset M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Head-Gordon, M.; Pople, J. A.; Frisch, M. *Chem. Phys. Lett.* **1988**, *153*, 503.

Table 3. Characteristic Structural Parameters of Norbornyl Cations **4a–d** (Bond Lengths, pm; Angles, deg, Calculated at MP2/6-311G(d,p), SDD (Sn, Pb) (See Also Figure 3) and Orbital Occupations (occ, au) According to NBO Theory

	E = Si (4a)	E = Ge (4b)	E = Sn (4c)	E = Pb (4d)
$r(\text{C}=\text{C})$	137.2	137.3	136.8	136.6
$r(\text{EC}6/7)$	235.2	244.1	267.2	280.6
ϵ	28.2	23.9	15.2	8.8
$\text{occ}(\pi(\text{C}=\text{C}))$	1.690	1.736	1.779	1.803
$\text{occ}(p(\text{E}))$	0.346	0.283	0.218	0.191

described in eq 2, show that the norbornyl cations **4a–d**



experience an additional stabilization compared to the Me_3E^+ cations by intramolecular interaction with the $\text{C}=\text{C}$ double bond ($24\text{--}18 \text{ kcal mol}^{-1}$). This results for the plumbanorbornyl cation **4d** in a calculated stabilization relative to *tert*-butyl cation of $-52.7 \text{ kcal mol}^{-1}$. Remarkably, the additional stabilization of the norbornyl cations relative to Me_3E^+ is reduced along the series **4a** > **4b**, **4c** > **4d**. This trend is paralleled by the decreasing intramolecular stabilization energy E_A for **4a–d**, which is the energy difference between the isomeric cations **6a–d** and the norbornyl cations **4a–d** (see Table 2).⁴⁹

In the calculated structures of **4a–d** the intramolecular interaction between the $\text{C}=\text{C}$ double bond and the element is clearly apparent (see Figure 3 and Table 3): (i) For all norbornyl cations the element– $\text{C}(6/7)$ distance, $r(\text{EC}(6/7))$, is markedly smaller than the sum of the van der Waals radii. (ii) The $\text{Me}_2\text{ECH}_2\text{--}$ group in **4a–d** is always clearly pyramidalized toward the $\text{C}=\text{C}$ double bond. The degree of pyramidalization is quantified by the angle ϵ , which is defined as the angle between the vector of the E–CH_2 bond and the plane spanned by the carbon atoms of the methyl groups and the element atom of the EMe_2 unit. (iii) The $\text{C}=\text{C}$ double bond in **4a–d** is predicted to be distinctively longer than calculated for the precursor silanes ($137.2\text{--}136.6 \text{ pm}$, **4a–d**; 133.6 pm , **6(H)a–d**), which is qualitatively consistent with electron transfer from the π -bonding orbital to the electron-deficient element atom. In agreement with this interpretation an NBO analysis⁴⁶ of the electron density reveals clearly depleted π -orbitals of the $\text{C}=\text{C}$ double bond (occupation number $\text{occ}(\pi(\text{C}=\text{C})) = 1.69\text{--}1.80$) and occupations for the formal empty p-orbitals at the element atom which differ decisively from zero ($\text{occ}(p(\text{E})) = 0.19\text{--}0.35$; see Table 3) for the norbornyl cations **4a–d**. Parallel to the attenuation of the intramolecular stabilization energy E_A in

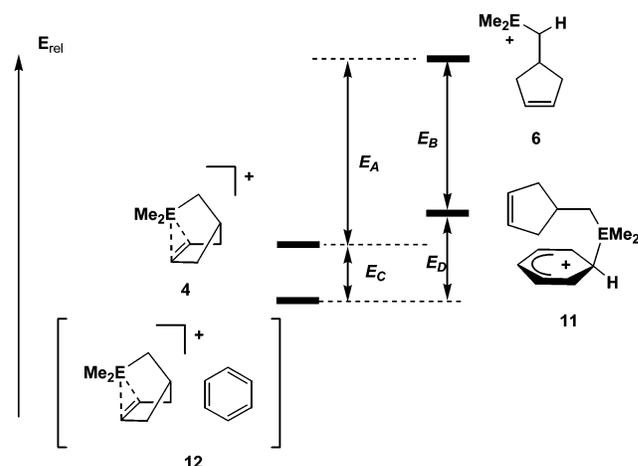


Figure 4. Energetic relation between the cations **4**, **6**, **11**, and **12** (see Table 4).

Table 4. Calculated Relative Energies $E_A\text{--}E_D$ (at B3LYP/6-311G(2d,p) (C, H), SDD (E)/B3LYP/6-31G(d) (C, H), SDD (E) + ΔZPVE) and Relative Free Enthalpies at 298 K, $G_A(298)\text{--}G_D(298)$, at B3LYP/6-31G(d) (C, H), SDD (E) for Cations **1–4** (kcal mol^{-1}) (See Also Figure 4)

E	E_A	$G_A(298)$	E_B	$G_B(298)$	E_C	$G_C(298)$	E_D	$G_D(298)$
Si	-19.5	-18.5	-17.1	-5.7	-4.1	5.3	-7.9	-7.6
Ge	-17.4	-16.2	-15.1	-3.5	-4.1	4.5	-6.4	-8.2
Sn	-17.0	-15.2	-16.4	-4.3	-3.4	7.4	-4.0	-3.5
Pb	-12.5	-10.8	-12.8	-0.9	-3.4	5.7	-3.1	-4.2

the series **4a** → **4d**, the geometric consequences arising from this interaction also decrease. That is, (i) the pyramidalization at the element, measured by the angle ϵ , is reduced and (ii) the $\text{C}=\text{C}$ double bond is calculated to be slightly shorter for the plumbanorbornyl cation **4d** than for the silication **4a**. Furthermore, the calculated charge transfer from the $\text{C}=\text{C}$ double bond to the element atom decreases continuously from the silication **4a** to the plumbanorbornyl cation **4d**, as shown by the calculated orbital occupations (see Table 3).

The comparison of the calculated interaction energy E_A with the reaction energy E_B to form the metalated benzenium ions **11a–c**^{50,51} reveals that the intramolecular transformation of the transient cations **6a–c** to give the norbornyl cations **4a–c** is energetically favored over the intermolecular reaction with benzene (see Figure 4 and Table 4). For the plumbium ion **6d**, E_B is slightly larger than E_A (by $0.3 \text{ kcal mol}^{-1}$). Entropy effects, however, clearly favor the formation of the norbornyl cation **4d** over the benzenium ion **11d** at ambient conditions (see Table 4), since the calculated thermal and free energy at 298 K ($G_B(298)$) to form **11d** is significantly smaller than $G_A(298)$ to form **4d**. The interaction energy E_C between benzene and the norbornyl cations **4a–d**,^{51,53} calculated for complexes **12a–d**, is relatively small (-3.4 to $-4.1 \text{ kcal mol}^{-1}$), and at

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(48) Similar results have been obtained for EX_3^+ ions (E = C–Pb, X = F–I): Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648.

(49) A somewhat different trend was computed for the intermolecular interaction between toluene and EX_3^+ ions (E = C–Pb, X = H, Me, Cl): Basch, H. *Inorg. Chim. Acta* **1996**, *242*, 191.

(50) The basis set superposition error for **11a** as estimated by a counterpoise calculation⁵² at the B3LYP/6-311G(2d,p)//B3LYP/6-31G(d) level of theory is $1.3 \text{ kcal mol}^{-1}$.

(51) This value must be regarded as a lower boundary, since the dispersion energy term of the intermolecular forces is not covered by hybrid density functionals as the here applied B3LYP functional. The dispersion energy term is, however, approximately 1 order of magnitude smaller than the here dominant ion–dipole interaction energy, and its absolute value is usually less than 2 kcal mol^{-1} . Hobza, P.; Šponer, J. Reschel, T. *J. Comput. Chem.* **1995**, *16*, 1315.

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Table 5. Calculated NMR Chemical Shifts of Norbornyl Cations **4a–f** (GIAO/B3LYP/6-311G(3d,p)/MP2/6-311G(d,p), SDD (Sn, Pb))

		$\delta(\text{E})$	$\delta(\text{C6/7})$	$\delta(\text{C4/5})$	$\delta(\text{C3})$	$\delta(\text{C2})$
4a	E = Si	92.6	160.5	47.1	44.7	18.2
	exptl	87.2	150.2	41.0	37.0	14.1
4b	E = Ge		157.5	46.5	45.3	24.9
	exptl ^b		144.8	40.4	36.5	18.2
4c	E = Sn		155.1	43.5	46.9	24.2
	exptl ^c		140.5	40.4	35.3	25.0
4d	E = Pb		152.0	46.1	45.9	42.8
	exptl ^d		138.0	38.2	36.5	53.4
4e	E = Si	81.3	159.5	47.2	44.4	15.0
	exptl	82.7	149.3	41.6	36.5	10.4
4f^e	E = Si	76.8	157.9	46.5	43.6	15.8
	exptl	80.2	149.6	41.6	36.6	12.7

^a Relative to calculated TMS: $\sigma(\text{Si, TMS}) = 325.2$. $\sigma(\text{C, TMS}) = 183.5$.

^b Experimental data for **4g**. ^c Experimental data for **4h**. ^d Experimental data for **4i**. ^e A geometry optimized at MP2/6-31G(d) was used.

298 K the formation of **12a–d** is endergonic ($G_{\text{C}}(298) > 0$). This negates the presence of significant solvent–cation interactions at room temperature and is in qualitative agreement with the negligible solvent effects on the element NMR and ¹³C NMR chemical shifts found experimentally (see Table 1).

At all applied levels of theory the β -element-substituted carbocations **9a–d** are not stationary points on the potential energy surface. The cations **9a–d** collapse during the optimization process to the symmetrical bridged norbornyl cations **4a–d**. This theoretical result discards a conceivable fast equilibrium between two β -element-substituted carbocations **9**, which is in line with the available experimental data. Further support for the bridged norbornyl cation nature of the observed species originates from quantum mechanical calculations of NMR chemical shifts. This method has been extensively applied in carbocation⁵⁴ and silyl cation^{2a,3c,d} chemistry, and the validity of theoretical structures is frequently established by comparing the computed NMR chemical shifts against the experimental data. The ²⁹Si and ¹³C NMR chemical shifts calculated for **4a–f** at GIAO/B3LYP/6-311G(3d,p)/MP2/6-311G(d,p) are summarized along with experimental data in Table 5.^{55a} The agreement between the calculated ²⁹Si NMR chemical shifts and the experimental data for the silacations **4a,e,f** is convincing; that is, the deviation $\Delta\delta_{\text{theor}}(^{29}\text{Si})$ is small ($\Delta\delta_{\text{theor}}(^{29}\text{Si}) = \delta(^{29}\text{Si})_{\text{calcd}} - \delta(^{29}\text{Si})_{\text{exptl}} < +6$). Thus, the ²⁹Si NMR chemical shift calculations for the silanorbornyl cations **4a,e,f** corroborate the validity of the computed structures. Surprisingly, the performance of this specific theoretical model for the calculations of ¹³C NMR chemical shifts is much less satisfactory. Although the general trend of the experimental ¹³C NMR chemical shifts is faithfully reproduced by the computations, the individual errors between computed and experimental ¹³C chemical shifts are large. In general all carbon nuclei are

calculated to be too deshielded, e.g., for **4a** by 4.1–10.3 ppm. In particular, the deviations for the vinylic carbons are large: +8.3–14.6. However, experimental and calculated ¹³C NMR chemical shift data are linearly correlated.^{55b} This indicates that the deviations are due to a systematic error, e.g., deficiencies of the applied method and basis set. DFT-based methods such as GIAO/DFT calculations are known to overestimate paramagnetic contributions to the chemical shielding, giving overly deshielded chemical shifts in critical cases for molecules with small HOMO/LUMO separations.^{3c,56} It has been demonstrated that the accurate calculation of the magnetic properties of alkenes, allenes, and unsaturated carbocations requires MP2 or even higher correlated methods, e.g., CCSD(T).^{57–60} The size of the cations studied and the extent of the present investigation however prevent the use of these highly accurate methods. The overall agreement between the theoretical and the experimental data (see Table 5) is however satisfying, when the reduced accuracy of the ¹³C NMR chemical shift calculations is taken into account.

Conclusion

Norbonyl cations **4** of the elements Si → Sn have been synthesized in aromatic hydrocarbon solutions by hydride-transfer reactions from cyclopentemethyl-substituted silanes, germanes, and stannanes (**5**) to trityl cation via transient trivalent element cations. In addition, the lead congener **4i** was obtained by treatment of the tetraalkyl-substituted plumbane **5i** with trityl cation. The cations **4** have been fully characterized by NMR spectroscopy, supported by quantum mechanical calculations of the structures, energies, and NMR chemical shifts. The experimental data as well as the theoretical results reveal the bridged structures of the cations **4**, with a formally pentacoordinated, positively charged element atom. Alternatively, the coordination of the element atom might be described as 3 + 1 coordination, with the unique binding side occupied by the C=C double bond. The cations **4** exhibit only negligible interactions with aromatic solvents and therefore can be regarded as “free cations” in solution. Addition of the stronger coordinating solvent acetonitrile to solutions of the norbornyl cations **4a,e–h** in aromatic hydrocarbons leads to a breakdown of the intramolecular interaction between the positively charged element and the C=C double bond and results in the formation of nitrilium ions with a tetracoordinated element atom. Although the interaction between the positively charged lead atom and the C=C double bond in the plumbanorbornyl cation **4i** is strongly influenced by addition of solvents of higher donor power, it endures, and with acetonitrile, the plumbyl cation **10i** with a trigonal bipyramidal coordinated lead center is formed in solution and in the solid state. The thermodynamic stability of the cations **4** and of the trimethyl-substituted element cation,

(53) The basis set superposition error for **12a** as estimated by a counterpoise calculation⁴⁸ at the B3LYP/6-311G(2d,p)/B3LYP/6-31G(d) level of theory is 0.8 kcal mol⁻¹.

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(55) (a) At this level the calculated ²⁹Si and ¹³C NMR chemical shifts for complexes between silyl cations and alkenes are converged, as can be shown by test calculations for [H₃Si/C₂H₄]⁺ optimized at MP2/6-311G(d,p): GIAO/B3LYP/6-311G(d,p), $\delta(^{29}\text{Si}) = -69.5$, $\delta(^{13}\text{C}) = 136.3$; GIAO/B3LYP/6-311G(2d,p), $\delta(^{29}\text{Si}) = -73.1$, $\delta(^{13}\text{C}) = 136.3$; GIAO/B3LYP/6-311G(2df,p), $\delta(^{29}\text{Si}) = -71.6$, $\delta(^{13}\text{C}) = 136.7$; GIAO/B3LYP/6-311G(3d,p) $\delta(^{29}\text{Si}) = -75.4$, $\delta(^{13}\text{C}) = 136.8$; GIAO/B3LYP/6-311G(3df,p), $\delta(^{29}\text{Si}) = -75.4$, $\delta(^{13}\text{C}) = 136.9$; GIAO/B3LYP/6-311G(3df,2p), $\delta(^{29}\text{Si}) = -74.2$, $\delta(^{13}\text{C}) = 136.9$. (b) $\delta_{\text{theor}}(^{13}\text{C}) = 1.05 \pm 0.02$, $\delta(^{13}\text{C}) = 3.7 \pm 1.5$, 24 data points, correlation coefficient 0.996; for details see the Supporting Information.

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Me_3E^+ , increases from Si to Pb. In contrast, the intramolecular stabilization energy E_A of the norbornyl cations decreases, suggesting reduced interaction between the C=C double bond and the electron-deficient element center in the plumbacations compared to the silacations. This points to a reduced electrophilicity of the plumbacation compared to its forerunners in group 14. This is in agreement with the computed orbital occupations for the cations and is experimentally supported by the reduced downfield shift of the vinylic carbon atoms C6/7 ($\Delta\delta(^{13}\text{C}) \approx 20$ (E = Si), $\Delta\delta(^{13}\text{C}) \approx 14$ (E = Ge), $\Delta\delta(^{13}\text{C}) \approx 11$ (E = Sn), $\Delta\delta(^{13}\text{C}) \approx 8$ (E = Pb)) along the series sila-, germa-, stanna-, and plumbanorbornyl cation.

Experimental Section

General Information. All reagents were obtained from commercial suppliers and were used without further purification. THF was distilled from sodium/potassium alloy/benzophenone. Benzene, benzene- d_6 , toluene, and toluene- d_8 were distilled from sodium. Acetonitrile was distilled from P_4O_{10} . Chlorosilanes and -germanes were distilled from CaH_2 . TFPFB was stored under vacuum for several hours prior to use. All reactions were carried out in oven-dried glassware under inert argon atmospheres. NMR spectra were recorded on Bruker AM-400 and DPX-250 instruments. ^1H NMR spectra were calibrated using residual nondeuterated solvents as internal reference, ^{13}C NMR spectra using the central line of the solvent signal. ^{29}Si NMR spectra were recorded using the INEPT pulse sequence. The ^{29}Si , ^{119}Sn , and ^{207}Pb NMR spectra were calibrated using external TMS ($\delta(^{29}\text{Si}) = 0.0$), $(\text{H}_5\text{C}_2)_4\text{Sn}$ ($\delta(^{119}\text{Sn}) = 1.8$), and $(\text{H}_5\text{C}_2)_4\text{Pb}$ ($\delta(^{207}\text{Pb}) = 71.0$), respectively. Chloromethyl-3-cyclopentene, **7**,⁶¹ 3-cyclopentenemethyldimethylsilane, **5a**,⁶¹ and TFPFB⁶² were prepared as described in the literature.

3-Cyclopentenemethyldichlorosilane. At -15°C , a solution of 3-cyclopentenemethylmagnesium chloride (50.2 mmol) in diethyl ether (30 mL) is slowly added to a vigorously stirred and cooled (-15°C) solution of trichlorosilane (20.35 g, 150.4 mmol) in diethyl ether (125 mL). The reaction mixture is stirred overnight and filtered through a glass frit. The residue is extracted once with dry diethyl ether (80 mL). The filtrates are combined, and the solvent is evaporated under reduced pressure. The oily residue is purified by vacuum distillation (40–42 $^\circ\text{C}$, 2 Pa) to give a pale pink oil (4.07 g, 44.92%). ^1H NMR (250.133 MHz, CDCl_3 , 303 K): δ 5.69 (s, 2H, $-\text{CH}=\text{CH}-$), 5.55 (t, 1H, $-\text{SiH}$, $^1J_{\text{Si,H}} = 277$ Hz, $^3J_{\text{H,SiH}} = 2.2$ Hz), 2.5–2.7 (m, 3H, $-\text{CH}_2\text{CHCH}_2-$), 1.98–2.17 (m, 2H, $-\text{CH}_2\text{CHCH}_2-$), 1.44 (dd, 2H, $-\text{CH}_2\text{Si}-$). ^{13}C NMR (62.860 MHz, CDCl_3 , 303 K): δ 129.8 (C6/7), 41.0 (C4/5), 32.3 (C3), 27.8 (C2). ^{29}Si NMR (79.460 MHz, CDCl_3 , 303 K): δ 10.2.

3-Cyclopentenemethyldi-*n*-butylchlorogermane. At -15°C , a solution of 3-cyclopentenemethylmagnesium chloride (3.3 mmol) in THF (100 mL) is slowly added to a vigorously stirred mixture of di-*n*-butyldichlorogermane (0.851 g, 3.3 mmol) and THF (1 mL). The solvent is evaporated under reduced pressure (2 Pa), and the residue is extracted twice with dry pentane (10 mL). After removal of pentane the oily product is purified by bulb-to-bulb distillation (85–95 $^\circ\text{C}$, 2 Pa). A colorless oil (0.58 g, 58%) is obtained. ^1H NMR (250.133 MHz, CDCl_3 , 303 K): δ 5.66 (s, 2H, $-\text{CH}=\text{CH}-$), 2.55–2.59 (m, 3H, $-\text{CH}_2\text{CHCH}_2-$), 1.99 (m, 2H, $-\text{CH}_2\text{CHCH}_2-$), 1.16–1.59 (m, 14H, $-\text{CH}_2\text{GeCH}_2\text{CH}_2\text{CH}_2-$), 0.90 (t, 6H, $-\text{CH}_3$). ^{13}C NMR (62.896 MHz, CDCl_3 , 303 K): δ 130.0 (C6/7), 41.7 (C4/5), 34.0 (C3), 26.9 (C2), 26.2, 25.8 ($-\text{GeCH}_2\text{CH}_2\text{CH}_2-$), 19.4 ($-\text{GeCH}_2\text{CH}_2-$), 13.6 ($-\text{CH}_3$).

3-Cyclopentenemethyldi-*n*-butylchlorostannane. At 0°C a solution of 3-cyclopentenemethylmagnesium chloride (34.35 mmol) in

diethyl ether (50 mL) is slowly added to a vigorously stirred solution of di-*n*-butyldichlorostannane (10.43 g, 34.35 mmol) in diethyl ether (80 mL). The reaction mixture is stirred for an additional day, and the solvent is evaporated under reduced pressure (2 Pa). The residue is extracted twice with dry pentane (20 mL). After removal of pentane the oily product is purified by vacuum distillation (101–103 $^\circ\text{C}$, 2 Pa) to give a colorless oil (7.1 g, 59.1%). ^1H NMR (250.133 MHz, CDCl_3 , 303 K): δ 5.68 (s, 2H, $-\text{CH}=\text{CH}-$), 2.8 (m, 1H, $-\text{CHCH}_2\text{Sn}-$), 2.51 (d, 2H, $-\text{CH}_2\text{CHCH}_2-$, $^2J_{\text{H,H}} = 15$ Hz), 1.94 (d, 2H, $-\text{CH}_2\text{CHCH}_2-$, $^2J_{\text{H,H}} = 15$ Hz), 1.47 (d, 2H, $-\text{CHCH}_2\text{Sn}-$, $^3J_{\text{H,H}} = 6$ Hz), 1.22–1.52 (m, 12H, $-\text{SnCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.92 (t, 6H, $-\text{CH}_3$). ^{13}C NMR (62.896 MHz, CDCl_3 , 303 K): δ 130.3 (C6/7), 42.1 (C4/5), 34.6 (C3), 28.0 ($-\text{CH}_2\text{CH}_3$), 26.8 ($-\text{SnCH}_2\text{CH}_2-$), 18.2 (C2), 13.6 ($-\text{CH}_3$), 13.5 ($-\text{SnCH}_2\text{CH}_2-$). ^{119}Sn NMR (93.181 MHz, CDCl_3 , 303 K): δ 139.3 ($-\text{SnCl}-$).

Triethyllead Bromide. At -80°C a solution of Br_2 (1.78 g, 11.26 mmol) in ethyl acetate (15 mL) is slowly added via a dropping funnel to a stirred solution of tetraethyllead (2 mL, 10.24 mmol) and ethyl acetate (10 mL). After addition of 1/3 of the Br_2 the colorless solution turns into a white suspension due to precipitated Et_3PbBr . The addition is stopped when the color of the reaction mixture remains yellow, which indicates a small excess of Br_2 . The cold reaction mixture is decanted off, and the white precipitate is extracted three times with 20 mL portions of diethyl ether at room temperature. The combined ethereal phases are evaporated and dried under reduced pressure (2 Pa) to give 1.14 g (30%) of a colorless crystalline solid. ^1H NMR (250.133 MHz, CDCl_3 , 303 K): δ 1.80 (t, 9H, $-\text{CH}_3$, $^3J_{\text{Pb,H}} = 177$ Hz), 2.21 (q, 6H, $-\text{CH}_2-$). ^{13}C NMR (62.860 MHz, CDCl_3 , 303 K): δ 34.3 ($-\text{CH}_2-$, $^1J_{\text{Pb,C}} = 191.9$ Hz), 13.0 ($-\text{CH}_3$, $^2J_{\text{Pb,C}} = 43.6$ Hz). ^{207}Pb NMR (52.304 MHz, CDCl_3 , 303 K): δ 513 (BrPbEt₃).

3-Cyclopentenemethyldiethylsilane (5e). Ethylmagnesium chloride (50.42 mmol) in dry diethyl ether (60 mL) is added to 3-cyclopentenemethyldichlorosilane (4.07 g, 22.5 mmol) in dry diethyl ether (50 mL). The reaction mixture is stirred for 30 min and is quenched with water/ NH_4Cl . The organic layer is separated, and the aqueous phase is washed four times with diethyl ether (80 mL). The combined organic layers are dried over MgSO_4 , and the solvent is removed. The oily residue is purified by distillation under reduced pressure (30–32 $^\circ\text{C}$, 2 Pa) to yield a colorless oil (2.85 g, 75.4%). ^1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.63 (s, 2H, $-\text{CH}=\text{CH}-$), 3.85 (m, 1H, $-\text{SiH}$, $^1J_{\text{Si,H}} = 179$ Hz), 2.48 (m, 2H, $-\text{CH}_2\text{CHCH}_2-$), 2.31 (m, 1H, $-\text{CH}-$), 1.94 (m, 2H, $-\text{CH}_2\text{CHCH}_2-$), 0.96 (t, 6H, $-\text{CH}_3$, $^3J_{\text{H,H}} = 7.9$ Hz), 0.75 (dd, 2H, $-\text{CHCH}_2\text{Si}-$, $^3J_{\text{H,H}} = 7.3$ Hz, $^3J_{\text{H,SiH}} = 3.2$ Hz), 0.60 (dq, 4H, $-\text{CH}_2\text{CH}_3$, $^3J_{\text{H,H}} = 7.9$ Hz, $^3J_{\text{H,SiH}} = 3.2$ Hz). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 130.3 (C6/7, $^1J_{\text{C,H}} = 162$ Hz), 42.3 (C4/5), 34.9 (C3), 18.9 (C2), 8.4 ($-\text{CH}_2\text{CH}_3$), 3.5 ($-\text{CH}_3$). ^{29}Si NMR (79.460 MHz, C_6D_6 , 303 K): δ -3.7.

3-Cyclopentenemethyldi-*n*-butylsilane (5f). *n*-Butylmagnesium chloride (9.84 mmol) in dry diethyl ether (25 mL) is added to 3-cyclopentenemethyldichlorosilane (0.89 g, 4.92 mmol). After being refluxed for 30 min the reaction mixture is quenched with water/ NH_4Cl . The organic layer is separated, and the aqueous phase is washed three times with diethyl ether (30 mL). The combined organic layers are dried over MgSO_4 , and the solvent is removed by rotary evaporation. Bulb-to-bulb distillation yields a colorless oil (0.79 g, 71.5%). ^1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.64 (s, 2H, $-\text{CH}=\text{CH}-$), 3.91 (m, 1H, $-\text{SiH}$, $^1J_{\text{Si,H}} = 178$ Hz, $^3J_{\text{H,SiH}} = 3.3$ Hz), 2.5 (dd, 2H, $-\text{CH}_2\text{CHCH}_2-$, $^2J_{\text{H,H}} = 14$ Hz, $^3J_{\text{H,H}} = 8$ Hz), 2.34 (m, 1H, $-\text{CH}-$), 1.96 (dd, 2H, $-\text{CH}_2\text{CHCH}_2-$, $^2J_{\text{H,H}} = 14$ Hz, $^3J_{\text{H,H}} = 7$ Hz), 1.35 (m, 4H, $-\text{CH}_2\text{CH}_3$), 1.34 (m, 4H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 0.9 (t, 6H, $-\text{CH}_3$, $^3J_{\text{H,H}} = 7$ Hz), 0.84 (dd, 2H, $-\text{CHCH}_2\text{Si}-$, $^3J_{\text{H,H}} = 7$ Hz, $^3J_{\text{H,SiH}} = 3.3$ Hz), 0.61 (m, 4H, $-\text{SiCH}_2\text{CH}_2-$). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 130.3 (C6/7, $^1J_{\text{C,H}} = 162$ Hz), 42.4 (C4/5), 35.0 (C3), 27.5 ($-\text{CH}_2\text{CH}_3$), 26.8 ($-\text{CH}_2\text{CH}_2\text{CH}_3$), 19.7 (C2), 14.0 ($-\text{CH}_3$), 11.8 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{29}Si NMR (79.460 MHz, C_6D_6 , 283 K): δ -9.2.

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3-Cyclopentenemethyl-*n*-butylgermane (5g). 3-Cyclopentene-methyl-*n*-butylchlorogermane (0.58 g, 1.91 mmol) is added to a solution of LiAlH₄ (0.247 g, 6.49 mmol) in diethyl ether (10 mL) and refluxed for 5 h. The reaction mixture is quenched with water, and Al(OH)₃ is dissolved in concentrated potassium/sodium tartrate solution. The organic layer is separated, and the aqueous phase is extracted three times with diethyl ether (10 mL). The combined organic layers are dried over MgSO₄, and the solvent is removed. Bulb-to-bulb distillation of the oily residue under reduced pressure (2 Pa) gives a colorless oil (0.37 g, 72%). ¹H NMR (250.133 MHz, CDCl₃, 303 K): δ 5.67 (s, 2H, -CH=CH-), 3.99 (septet, 1H, -GeH, ³J_{H,H} = 3.1 Hz), 2.52 (m, 2H, -CH₂CHCH₂-), 2.4 (m, 1H, -CH-), 1.98 (m, 2H, -CH₂-CHCH₂-), 1.37–1.38 (m, 8H, -GeCH₂CH₂CH₂CH₃), 0.99 (dd, 2H, -CHCH₂Ge-, ²J_{H,H} = 7.2 Hz, ³J_{H,H} = 3.2 Hz), 0.9 (t, 6H, -CH₃, ³J_{H,H} = 6.9 Hz), 0.82 (m, 4H, -GeCH₂CH₂-). ¹³C NMR (62.896 MHz, CDCl₃, 303 K): δ 130.2 (C6/7, ¹J_{C,H} = 161 Hz), 42.2 (C4/5), 36.1 (C3), 28.9 (-CH₂CH₃), 26.4 (-GeCH₂CH₂-), 20.4 (C2), 14.0 (-CH₃), 12.5 (-GeCH₂CH₂-).

3-Cyclopentenemethyl-*n*-butylstannane (5h). At -10 °C a solution of LiEt₃H (6 mmol) in THF (6 mL) is slowly added to a stirred solution of 3-cyclopentenemethyl-*n*-butylchlorostannane (1.475 g, 4.22 mmol) in diethyl ether (20 mL). The reaction mixture is allowed to warm to room temperature and is stirred for an additional 8 h. The mixture is quenched with water, and the organic layer is separated. The aqueous phase is extracted three times with diethyl ether (20 mL). The combined organic layers are dried over MgSO₄, and the solvent is removed under vacuum (2 Pa). The oily residue is flash-distilled at 2 Pa using a preheated oil bath (160 °C) to give a colorless oil (1 g, 75%). ¹H NMR (250.133 MHz, C₆D₆, 303 K): δ 5.65 (s, 2H, -CH=CH-), 5.03 (septet, 1H, -SnH, ¹J_{Sn,H} = 1587 Hz, ³J_{H,H} = 2 Hz), 2.53 (m, 3H, -CH₂CHCH₂-), 1.94 (m, 2H, -CH₂CHCH₂-), 1.1 (dd, 2H, -CHCH₂Sn-, ³J_{H,H} = 6.9 Hz, ³J_{H,SnH} = 2 Hz), 0.8–1.6 (m, 12H, -CH₂CH₂CH₂CH₃), 0.91 (m, 6H, -CH₃, ³J_{H,H} = 7.2 Hz). ¹³C NMR (62.896 MHz, C₆D₆, 303 K): δ 130.4 (C6/7, ¹J_{C,H} = 161 Hz), 43.1 (C4/5), 36.9 (C3), 30.3 (-CH₂CH₃), 27.4 (-SnCH₂CH₂-), 17.4 (C2), 13.7 (-CH₃), 8.7 (-SnCH₂CH₂-). ¹¹⁹Sn NMR (93.181 MHz, C₆D₆, 303 K): δ -9.1 (-SnH).

3-Cyclopentenemethyltriethylplumbane (5i). A solution of 3-cyclopentenemethylmagnesium chloride (18.1 mmol) in diethyl ether (30 mL) is added via a Teflon tube to solid Et₃PbBr (6.77 g, 18.1 mmol). The resulting brown slurry is stirred for 1/2 h. The solvent is removed under vacuum (2 Pa), and the residue is extracted twice with pentane (20 mL). The combined organic layers are evaporated under reduced pressure (2 Pa) to give a brown oil. Bulb-to-bulb distillation yields a colorless oil (3.4 g, 50%). ¹H NMR (250.133 MHz, C₆D₆): δ 5.64 (s, 2H, -CH=CH-), 2.68 (m, 1H, -CH-, ³J_{H,H} = 7.3 Hz), 2.51 (dd, 2H, -CH₂CHCH-, ²J_{H,H} = 14.4 Hz), 1.89 (dd, 2H, -CH₂CHCH₂-, ²J_{H,H} = 14.4 Hz, ³J_{H,H} = 5.9 Hz), 1.64 (d, 2H, -CHCH₂Pb-, ³J_{H,H} = 7.3 Hz), 1.46 (s, 15H, -CH₂CH₃), 1.46 (s, 15H, -CH₃). ¹³C NMR (62.896 MHz, C₆D₆, 303 K): δ 130.2 (C6/7, ¹J_{C,H} = 161.2 Hz), 43.8 (C4/5, ³J_{Pb,C} = 56.8 Hz), 38.4 (C3, ²J_{Pb,C} = 28.6 Hz), 27.0 (C2, ¹J_{Pb,C} = 183.2 Hz), 14.0 (-CH₃, ²J_{Pb,C} = 30.5 Hz), 10.4 (-CH₂CH₃, ¹J_{Pb,C} = 188.8 Hz). ²⁰⁷Pb NMR (52.304 MHz, C₆D₆, 303 K): δ 50.5.

2-Norbonyl Cations 4. Slow addition of the precursor **5** (0.5 mmol) to a vigorously stirred solution of TPFPB (461 mg (0.5 mmol) in benzene-*d*₆ (3 mL)) at room temperature results in a slightly exothermic reaction. The reaction is finished when the color of the trityl cation has disappeared. Stirring is stopped, and the reaction mixture is allowed to separate into two layers, a dark red lower phase and a colorless to slightly yellow upper phase. The upper layer, which contains the byproduct triphenylmethane, is separated off, and the lower layer is transferred via a flexible Teflon pipe into an NMR tube and is investigated by NMR spectroscopy. Evaporation of the solvent in a vacuum and washing of the oily residue with 2 mL portions of pentane gives the solid salts.

2,2-Dimethyl-2-silanorbonyl Cation (4a). Red glassy powder, 286 mg, 70% yield. ¹H NMR (250.133 MHz, C₆D₆, 298 K): δ 5.84 (s, 2H, -CH=CH-), +2.50 to -0.29 (m, 48H, (-CH₂)₂CHSi(CH₃)). ¹³C NMR (62.896 MHz, C₆D₆, 289 K): δ 150.6 (C6/7, ¹J_{C,H} = 170.4 Hz), 41.4 (C4/5), 37.4 (C3), 14.5 (C2), -2.2 (-CH₃). ²⁹Si NMR (79.460 MHz, C₆D₆, 298 K): δ 87.2.

2,2-Diethyl-2-silanorbonyl Cation (4e). Red oil, 253 mg, 60% yield. ¹H NMR (400.136 MHz, C₆D₆, 283 K): δ 5.92 (s, 2H, -CH=CH-), 2.23 (t, 1H, -CH-, ³J_{H,H} = 2.4 Hz), 1.61 (dm, 2H, -CH₂-CHCH₂-, ²J_{H,H} = 15.9 Hz), 1.41 (d, 2H, -CH₂CHCH₂-, ²J_{H,H} = 15.9 Hz), 0.57 (t, 6H, -CH₃, ³J_{H,H} = 7.5 Hz), 0.35 (q, 4H, -CH₂CH₃, ³J_{H,H} = 7.5 Hz), 0.00 (d, 2H, -CHCH₂Si-, ³J_{H,H} = 2.4 Hz). ¹³C NMR (100.614 MHz, C₆D₆, 300 K): δ 149.8 (C6/7, ¹J_{C,H} = 173 Hz), 41.6 (C4/5, ¹J_{C,H} = 139 Hz), 36.5 (C3, ¹J_{C,H} = 147 Hz), 10.4 (C2, ¹J_{C,H} = 137 Hz), 6.1 (-CH₃, ¹J_{C,H} = 139 Hz), 5.3 (-CH₂CH₃, ¹J_{C,H} = 128 Hz). ²⁹Si NMR (79.460 MHz, C₆D₆, 283 K): δ 82.7.

2,2-Di-*n*-butyl-2-silanorbonyl Cation (4f). Red oil, 293 mg, 65% yield. ¹H NMR (250.133 MHz, C₆D₆, 303 K): δ 6.00 (s, 2H, -CH=CH-), 2.22 (m, 1H, -CH₂CHCH₂-, ³J_{H,H} = 3.4 Hz), 1.62 (dd, 2H, -CH₂CHCH₂-, ²J_{H,H} = 16 Hz, ³J_{H,H} = 3.4 Hz), 1.40 (d, 2H, -CH₂-CHCH₂-, ²J_{H,H} = 16 Hz), 0.83–1.07 (2m, 8H, -SiCH₂CH₂-), 0.77 (t, 6H, -CH₃, ³J_{H,H} = 7.3 Hz), 0.45 (m, 4H, -CH₂CH₃), 0.04 (d, 2H, -CHCH₂Si-, ³J_{H,H} = 2.9 Hz). ¹³C NMR (62.860 MHz, C₆D₆, 303 K): δ 149.6 (C6/7, ¹J_{C,H} = 174 Hz), 41.6 (C4/5), 36.6 (C3), 25.4 (-SiCH₂CH₂-), 24.9 (-CH₂CH₃), 13.0 (-SiCH₂CH₂-), 12.7 (C2), 12.6 (-CH₃). ²⁹Si NMR (79.460 MHz, C₆D₆, 283 K): δ 80.2.

2,2-Di-*n*-butyl-2-germanorbonyl Cation (4g). Red oil, 307.6 mg, 65% yield. ¹H NMR (250.133 MHz, C₆D₆, 303 K): δ 5.76 (s, 2H, -CH=CH-), 2.36 (m, 1H, -CH₂CHCH₂-), 1.61 (dd, 2H, -CH₂-CHCH₂-, ²J_{H,H} = 15.8 Hz, ³J_{H,H} = 4.4 Hz), 1.30 (d, 2H, -CH₂-CHCH₂-, ²J_{H,H} = 15.8 Hz), 0.80–1.15 (m, 12H, -GeCH₂CH₂CH₂-), 0.77 (t, 6H, -CH₃, ³J_{H,H} = 7.0 Hz), 0.44 (d, 2H, -CHCH₂Ge-, ³J_{H,H} = 2.9 Hz). ¹³C NMR (62.860 MHz, C₆D₆, 303 K): δ 144.8 (C6/7, ¹J_{C,H} = 173.2 Hz), 40.4 (C4/5), 36.5 (C3), 25.8 (-CH₂CH₃), 24.8 (-GeCH₂CH₂-), 18.5 (-GeCH₂CH₂-), 18.2 (C2), 12.4 (-CH₃).

2,2-Di-*n*-butyl-2-stannanorbonyl Cation (4h). White powder, 382.1 mg, 77% yield. ¹H NMR (250.133 MHz, C₆D₆, 303 K): δ 5.54 (s, 2H, -CH=CH-), 2.70 (m, 1H, -CH₂CHCH₂-, ³J_{Sn,H} = 183 Hz), 1.79 (dd, 2H, -CH₂CHCH₂-, ²J_{H,H} = 15.3 Hz, ³J_{H,H} = 4.6 Hz), 1.27 (d, 2H, -CH₂CHCH₂-, ²J_{H,H} = 15.3 Hz), 0.85–1.20 (m, 12H, -SnCH₂CH₂CH₂-), 0.81 (t, 6H, -CH₃, ³J_{H,H} = 7.0 Hz), 0.68 (d, 2H, -CHCH₂Sn-, ³J_{H,SnH} = 3.0 Hz). ¹³C NMR (62.860 MHz, C₆D₆, 303 K): δ 141.5 (C6/7, ¹J_{C,H} = 170 Hz, ¹J_{Sn,C} = 26 Hz), 40.4 (C4/5), 35.3 (C3), 27.6 (-SnCH₂CH₂-, ²J_{Sn,C} = 27.9 Hz), 26.2 (-CH₂CH₃, ³J_{Sn,C} = 75 Hz), 25.0 (C2), 19.9 (-SnCH₂CH₂-, ¹J_{Sn,C} = 256 Hz), 12.4 (-CH₃). ¹¹⁹Sn NMR (93.181 MHz, C₆D₆, 303 K): δ 334.

2,2-Diethyl-2-plumbanorbonyl Cation (4i). Slow addition of **5i** (193 mg, 0.515 mmol) to a vigorously stirred solution of TPFPB (0.461 g, 0.5 mmol) in dry C₆D₆ (3 mL) results in evolution of ethene²⁴ and the disappearance of the red color of the solution. The reaction mixture is allowed to separate into two layers, an upper colorless layer and a lower light brown layer. The upper layer contains the byproduct triphenylmethane and is removed. The lower phase is transferred via a flexible Teflon pipe into an NMR tube. After evaporation of the solvent in a vacuum and washing of the oily residue with 2 mL portions of pentane, a white crystalline powder is obtained (486.9 mg, 95% yield). ¹H NMR (250.133 MHz, C₆D₆, 303 K): δ 5.29 (s, 2H, -CH=CH-), 4.41 (m, 1H, -CH-, ³J_{Pb,H} = 333 Hz), 2.07 (dd, 2H, -CH₂CHCH₂-, ²J_{H,H} = 15.5 Hz, ³J_{H,H} = 5.5 Hz), 1.80 (br, 4H, -CH₂CH₃), 1.62 (t, 6H, -CH₃, ³J_{H,H} = 7.5 Hz), 1.51 (d, 2H, -CHCH₂Pb-, ³J_{H,H} = 2.9 Hz), ²J_{Pb,H} = 21 Hz), 1.35 (d, 2H, -CH₂CHCH₂-, ²J_{H,H} = 15.5 Hz). ¹³C NMR (62.860 MHz, C₆D₆, 303 K): δ 138.0 (C6/7, ¹J_{Pb,C} = 16.2 Hz, ¹J_{C,H} = 170 Hz), 53.4 (C2, ¹J_{Pb,C} = 36.6 Hz), 39.3 (C4/5, ³J_{Pb,C} = 44.2 Hz), 38.2 (-CH₂CH₃, ¹J_{Pb,C} = 36.7 Hz), 36.5 (C3, ²J_{Pb,C} = 46.2 Hz), 12.0 (-CH₃, ²J_{Pb,C} = 41.4 Hz). ²⁰⁷Pb NMR (52.304 MHz, C₆D₆, 303 K): δ 1049.

Nitrilium Ions 10. Addition of 1 equiv of dry acetonitrile (20.5 mg, 0.5 mmol) via a syringe to a solution of the norbornyl cation (0.5 mmol) in C_6D_6 (1.5 mL) gave a deep red solution of the corresponding nitrilium ion **10**, which was investigated by NMR spectroscopy.

(3-Cyclopentenemethyldimethylsilyl)acetonitrilium (10a). 1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.56 (s, 2H, $-CH=CH-$), 2.47–2.21 (m, 3H, $-CH_2CHCH_2-$), 1.69 (dd, 2H, $^2J_{H,H} = 13.2$ Hz, $^3J_{H,H} = 6.2$ Hz, $-CH_2CHCH_2-$), 0.99 (br, m, 2H, $-CHCH_2Si$), 0.37 (s, 6H, $-SiCH_3$). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 130.0 (C6/7), 41.4 (C4/5), 32.6 (C3), 21.8 (C2), -2.5 ($-CH_3$), ^{29}Si NMR (79.460 MHz, C_6D_6 , 283 K): δ 31.8.

(3-Cyclopentenemethyldiethylsilyl)acetonitrilium (10e). 1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.57 (s, 2H, $-CH=CH-$), 2.32 (m, 2H, $-CH_2CHCH_2-$), 2.13 (br m, 1H, $-CH_2CHCH_2-$), 1.69 (d, 2H, $-CH_2CHCH_2-$, $^2J_{H,H} = 14.8$ Hz), 0.77 (br m, 6H, $-CH_3$), 0.54 (br m, 4H, $-CH_2CH_3$), 0.22 (br m, 2H, $-CHCH_2Si-$). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 129.5 (C6/7, $^1J_{C,H} = 159.3$ Hz), 120.5 (NCCH₃), 41.0 (C4/5), 32.1 (C3), 17.8 (C2), 5.2 ($-CH_3$), 3.7 ($-CH_2CH_3$), -0.4 (NCCH₃). ^{29}Si NMR (79.460 MHz, C_6D_6 , 283 K): δ 37.5.

(3-Cyclopentenemethyldi-*n*-butylsilyl)acetonitrilium (10f). 1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.55 (s, 2H, $-CH=CH-$), 0.50–2.50 (br m, $-(CH_2)_2CHCH_2SiCH_2CH_2-$), 0.56 (m, 4H, $-CH_2-CH_3$), 0.83 (t, 6H, $-CH_3$, $^3J_{H,H} = 7.3$ Hz). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 130.7 (C6/7), 41.0 (C4/5), 32.0 (C3), 25.4 ($-SiCH_2CH_2-$), 23.8 ($-SiCH_2CH_2-$), 18.7 (C2), 12.5 ($-CH_3$), 10.9 ($-CH_2CH_3$), -0.9 (NCCH₃). ^{29}Si NMR (79.460 MHz, C_6D_6 , 283 K): δ 37.5.

(3-Cyclopentenemethyl-di-*n*-butylgermyl)acetonitrilium (10g). 1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.42 (s, 2H, $-CH=CH-$), 2.25 (br m, 3H, $-CH_2CHCH_2-$), 1.59 (d, $-CH_2CHCH_2-$, $^2J_{H,H} = 13.9$ Hz), 0.80–1.30 (4m, 14H, $-CHCH_2GeCH_2CH_2CH_2CH_3$), 0.81 (t, 6H, $-CH_3$, $^3J_{H,H} = 7.1$ Hz). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 130.6 (C6/7), 118.7 (br, NCCH₃), 40.2 (C4/5), 33.2 (C3), 25.7, 25.1, 17.5 ($-CH_2CH_2CH_2CH_3$), 24.6 (C2), 12.6 ($-CH_3$), -0.8 (NCCH₃).

(3-Cyclopentenemethyl-di-*n*-butylstannyl)acetonitrilium (10h). 1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.44 (s, 1H, $-CH=CH-$), 5.69 (s, 1H, $-CH=CH-$), 2.72–2.81 (2m, 1H, $-CH_2CHCH_2-$), 1.94 (m, 2H, $-CH_2CHCH_2-$), 1.36 (m, $-CH_2CHCH_2-$), 0.80–1.30 (m, 20H, $-CH_2CH_2CH_2-$), 0.87 (t, 6H, $-CH_3$, $^3J_{H,H} = 3.6$ Hz), 0.77–

0.82 (2d, 2H, $-CHCH_2Sn-$, $^3J_{H,H} = 2.8$ Hz). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 130.7 (C6/7), 117.9 (NCCH₃), 42.5 (C4/5), 35.1 (C3), 28.3 ($-SnCH_2CH_2-$, $^2J_{Sn,C} = 30$ Hz), 26.9 ($-CH_2CH_3$, $^3J_{Sn,C} = 75.5$ Hz), 19.5 (C2), 19.5 ($-SnCH_2CH_2-$), 13.3 ($-CH_3$), -0.3 (NCCH₃). ^{119}Sn NMR (93.181 MHz, C_6D_6 , 283 K): δ 54.4.

(3-Cyclopentenemethyldiethylplumbyl)acetonitrilium (10i). Single crystals suitable for X-ray crystallography are grown in dry pentane in a sealed ampule at 40 °C for several weeks (solvothermal conditions). 1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 5.47 (m, 2H, $-CH=CH-$), 1.30–2.50 (4m, $(-CH_2)_2CHCH_2PbCH_2-$), 1.75 (t, $-CH_3$, $^3J_{H,H} = 7.6$ Hz). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 131.7 (C6/7), 117.2 (NCCH₃), 49.1 (C2), 40.9 ($-CH_2CH_3$), 35.6 (C3), 34.3 (C4/5), 12.0 ($-CH_3$), -0.9 (NCCH₃). ^{207}Pb NMR (52.304 MHz, C_6D_6 , 303 K): δ 598.

Triethylplumbylbenzenium Ion. Slow addition of tetraethyllead (161.5 mg, 0.5 mmol) to a vigorously stirred solution of TPFPPB (0.461 g, 0.5 mmol) in dry C_6D_6 (3 mL) results in evolution of ethene²⁴ and the disappearance of the red color of the solution. The reaction mixture is allowed to separate into two layers, an upper colorless layer and a lower light brown layer. The upper layer contains the byproduct triphenylmethane and is removed. The lower phase is transferred via a flexible Teflon pipe into an NMR tube. 1H NMR (250.133 MHz, C_6D_6 , 303 K): δ 1.82 (t, 9H, $-CH_3$, $^3J_{Pb,H} = 173.2$ Hz, $^3J_{H,H} = 7.7$ Hz), 1.71 (m, 6H, $-CH_2-$). ^{13}C NMR (62.860 MHz, C_6D_6 , 303 K): δ 46.9 (br, $-CH_2-$), 11.1 ($-CH_3$, $^2J_{Pb,C} = 38.4$ Hz). ^{207}Pb NMR (52.304 MHz, C_6D_6 , 303 K): δ 1432 (**10i**).

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Supporting Information Available: Table of computed absolute energies, figure of $\delta_{theor}(^{13}C)$ vs $\delta(^{13}C)(exptl)$, crystallographic data of compound **10i**, NMR spectra of cations **4a**–**h**, and Cartesian coordinates for the optimized geometries of cations **4a**–**f**, **6a**–**d**, **11a**–**d**, and **12a**–**d** (PDF) and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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